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In-situ WAXS Studies of Structural Changes in Wood Foils and in Individual Wood Cells During Microtensile Tests

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Introduction

The distinctive mechanical qualities of biological materials can be directly attributed to their *hierarchical architecture* with a variety of compositional, structural and dimensional units [1]. Moreover, the recent *in-situ* studies of nacre and bone have indicated also the important role of *molecular interactions* and bond recovery phenomena operating at the nanometer level [2]. The molecular mechanistic phenomena are responsible for various stiffness recovery effects at molecular and submolecular levels and originate in deformability, folding, branching, interfacial interaction and compositional variability of polymers in the biological structures [1,2].

Wood is also a complex, hierarchically structured, polymer-like material based on fibrils of crystalline cellulose and amorphous matrix of lignin and hemicelluloses. In comparison with artificial materials, wood exhibits a remarkably good mechanical performance when taking its low density into consideration [3]. There has been a significant effort to characterize the structural and mechanical properties of various wood tissue types using numerous experimental techniques and modelling approaches with an aim to understanding the contribution of the lowest hierarchical units to the mechanical performance of the tissue [4,5]. It has been demonstrated by several authors that the mechanical properties of wood are significantly influenced by fibrils of crystalline cellulose wound in the form of a Z-Helix around the lumen [6-10]. The tilt angle of the cellulose fibrils in the S2-layer versus the longitudinal cell axis (usually called microfibril angle [MFA]) plays an important role in determining the actual stiffness of wood.

When investigating the properties of wood, one of the main difficulties is the compositional, architectural and dimensional variability of the tissue constituents originating in the hierarchical nature of the material. The understanding of structure-property relationships in wood thus requires use of complex characterization techniques which probe the properties and role of various tissue constituents as well as their interaction. In-situ deformation experiments combined with structural characterization represent a powerful methodological tool to characterize properties of complex materials. In this work, results from synchrotron wide-angle X-ray scattering (WAXS) experiments on thin wood foils and on individual wood cells combined with tensile tests are reported. The main goal of these simultaneous structural and mechanical investigations on wood foils and wood cells was to (i) *characterize structural changes* in the tissues at different stages of the tensile experiments and to (ii) *separate deformation mechanisms* inside the cell-wall from those mediated by cell-cell interactions. The results indicate the presence of a re-stiffening mechanism in the cell wall, which was related to the properties of the amorphous polymer cell constituents [11,12].

Materials and Methods

From compression wood of *Ginkgo biloba* L., *Juniperus virginiana* L. and *Picea abies* [L.] Karst., tangential sections with dimensions of 50 x 5 x 0.2 mm³ and individual cells of 20-30 μm in diameter and 1-1.5 mm in length were prepared. The individual wood cells were isolated mechanically using very fine tweezers in order not to modify the chemical and the structural properties of the cell wall [13]. The application of this isolation technique allowed study of the mechanical behaviour of the unmodified cell wall and made it possible to evaluate the contribution of the distinct cell wall components to the mechanical behaviour of the intact tissue.

The tissues were characterised using *in-situ* diffraction

experiments performed at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France (Fig. 1). The foils as well as the cells were investigated in transmission geometry with the X-ray beam perpendicular to the cell axis. For the investigations on foils, a tensile stage developed by the authors was delivered to the ID1 beamline before the experiment. The computer-controlled stage allowing the measurement of sample elongation and force applied on the sample was inserted in the goniometer. The beam of 0.5 mm in diameter was used and the scattering signal was collected using a two-dimensional (2D) CCD detector. The wood foils were strained in a tensile stage under various strain rates monitoring stress response and structural changes.

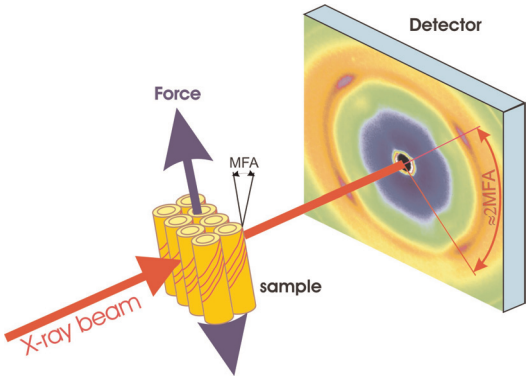

Figure 1. A schematic description of the in-situ synchrotron WAXS. A wood foil (or a single wood cell) was strained in a tensile stage while the structural changes were monitored using the 2D CCD detector in transmission geometry. After the measurement, the MFA magnitudes were evaluated from the WAXS data for different stages of the tensile experiment and, subsequently, the mechanical and the structural values were correlated.

In the case of individual cells, the characterization was performed at the ESRF microfocus beamline ID13 with a beam of 2 μm diameter. The cells were tested in a piezoelectric stretching device provided by the ESRF working with a rate of 500 nm/s. As in the case of foils, the mechanical data (such as force applied on the cell and the cell elongation) and the structural changes (characterized using the 2D CCD detector) were monitored.

By relating the stress-strain curves and scattering results, it was possible to evaluate changes of the MFA as a function of external strain and the strain rate in the tissues. The magnitudes of the MFA were evaluated from cellulose 200 reflections as described in Ref. 8.

Results and Discussion

Figure 2 presents typical WAXS patterns collected at the beginning and the end of the tensile experiments on a foil of *Picea*. In Fig. 3, distributions of the intensity along *cellulose* 200 Debey-Scherrer rings obtained by the integration of the WAXS patterns (Fig. 2) are presented. The results indicate a change of the MFA from 43° to 30°. The

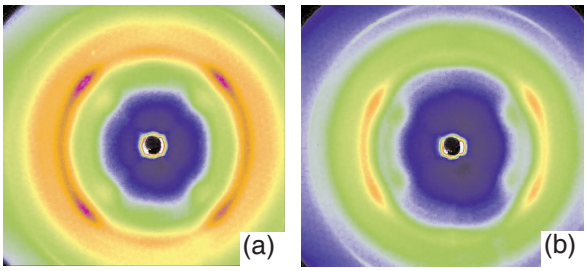

Figure 2. Results from WAXS on a foil of Picea. The patterns (a) and (b) collected at the beginning and at the end of the in-situ experiment, respectively, demonstrate a decrease of MFA in the foil.

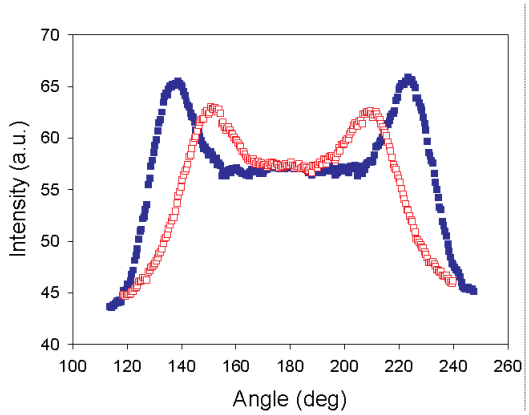

Figure 3. Results from WAXS on a foil of Picea. Filled and empty symbols represent integrated data from Fig. 2a and b, respectively. The data demonstrate a decrease of MFA in the foil from 43° to 30° due to straining.

MFA magnitude was evaluated for different stages of the tensile experiments and the mechanical data were correlated with the structural changes, namely with the development of the MFA in the tissues. In Figs. 4,5 mechanical and structural results obtained from foils and cell of *Picea* are presented.

In the case of the foil (Fig. 4a,b), the mechanical behaviour was decisively influenced by the magnitude of MFA in the unstressed state [4,5]. During the initial period of testing, the tissues exhibited a relatively high stiffness. In the plastic region, however, when the straining was interrupted, the original stiffness was recovered after reloading. With an additional increase in the strain, the region with lower stiffness was reached again.

The analysis of the structural data from foils (Figs. 4a,b) documents that the MFA decreases when the strain increases [11]. The MFA magnitude can be related to the actual value of the strain and is not influence by the strain rate. Even at zero strain rates, the MFA does not change significantly. The MFA dependence on strain can be approximately described by the equation:

$$MFA(\varepsilon) = MFA(0) - cotg[MFA(0)]\ \varepsilon. \qquad (1)$$

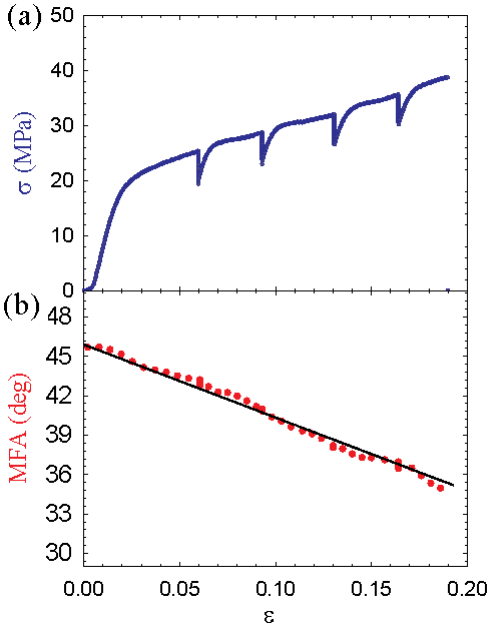

Figure 4. Mechanical and structural data from in-situ WAXS experiments on a foil of Picea. The stress-strain curve in (a) documents that the straining of the foil was interrupted four times. In (b) the corresponding dependence of the MFA as a function the strain is depicted by points. The solid line in (b) represents a theoretical dependence of the MFA on the strain calculated on the basis of the model introduced in Ref 11 (Eq. 1).

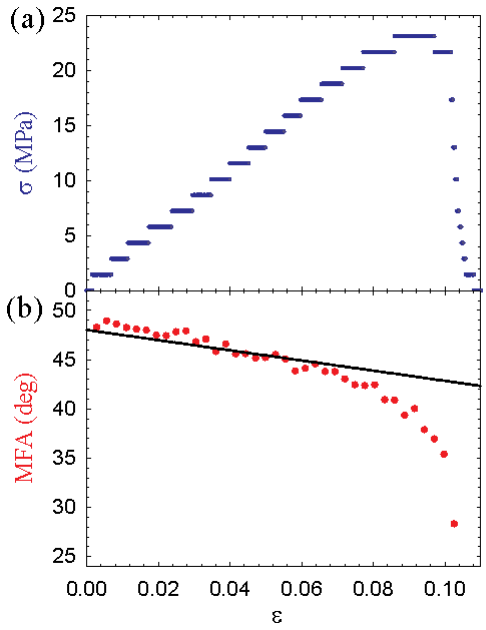

Figure 5. Mechanical (a) and structural (b) data from in-situ WAXS experiments on a single cell of Picea. The solid line in (b) represents a theoretical dependence of MFA on the strain calculated on the bases of the model introduced in Ref 11 (Eq. 1).

In the case of *in-situ* tests on individual cells, structural and mechanical behaviour similar to that in foils was observed. The results in Fig. 5a,b document a decrease of MFA in a cell of *Picea* that broke at relatively low strain. The main difference in the behaviour of the foils and the cells was that the deformation in single cells was not uniform over the length of the cell. In some regions the deformation could be exceedingly large (reducing the MFA almost down to zero) while other regions of the cell were less deformed. The results in Fig. 5a,b indicate that, close to the fracture, the MFA in the cell decreased and did not follow the dependence predicated by Eq. 1. In further cyclic loading tests in laboratory conditions (performed without X-ray radiation) individual cells and foils exhibited a similar stress-strain behaviour as the tissues examined during in-situ WAXS experiments [11].

The interpretation of the experimental data indicates that the mechanical behaviour of wood is influenced by the magnitude of the MFA and an additional mechanism responsible for the stiffness recovery beyond the yield point. This mechanism is not likely to originate in crystalline cellulose and must therefore be connected with the amorphous constituents of the cell wall [12]. It is supposed that the re-stiffening effect under cyclic loading originates in the bond recovery occurring in the amorphous matrix between the helical cellulose microfibrils [11,12]. As in the case of nacre and bone, this phenomenon governs the formation and breaking of polymer cross-links in the cell wall and, in this way, provides a plastic-like behaviour to the biological material. It can be supposed that this "Velcro-like" behaviour could be mediated by the hemicelluloses attached to the cellulose fibrils [11,12]. However, further investigations are necessary to fully understand the mechanical interaction of the polymers in the cell wall.

Acknowledgements

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